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POWDER DIFFRACTION I & II*

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POWDER DIFFRACTION I*

During World War I scientists in two different parts of the world independently discovered that there existed a characteristic x-ray diffraction effect from a fine -grained crystalline aggregate. This discovery was made by DEBYE and SCHERRER in Germany and almost simultaneously by HULL in the United States.

Although much information is lost or degraded by using an aggregate in place of a single crystal, this method of investigating crystals has proved to be exceedingly useful in those cases where single crystals are not available, are difficult to obtain or one wishes to examine a crystalline material which is not in the form of discrete single crystal, for example, a metal.

There are many applications of the powder method, but two of these are of primary importance. Fundamentally, the powder method provides a way of investigating, within limits, the crystallography of the crystal in the powder. Secondly, since the powder diffraction diagram produced by a crystalline substance is a characteristic of that substance, the powder method can be used as a means of identification of crystals.

Each crystal may be envisaged as a reciprocal lattice. Since an ideal polycrystalline material or powder is an ensemble of a very large number of randomly oriented crystallites the reciprocal lattices associated with them are randomly oriented also. The origins of all these lattices, however, lie at the point where the direct beam leaves the sphere of reflection.

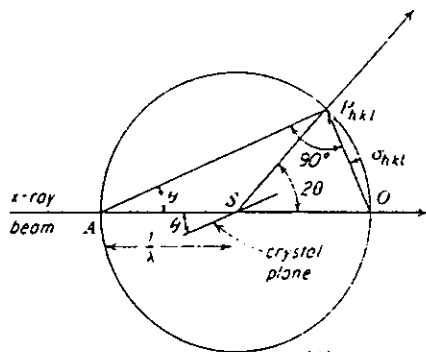


Fig. 1. (11)

Consider the reciprocal-lattice point hkl at the end of the vector σ_{hkl} in Fig.1. If there is an infinite number of crystals in the powder, there must be an infinite number of such points hkl , all lying at a vector distance σ_{hkl} from the origin. Since these vectors are randomly directed in space, the reciprocal-lattice points hkl must lie on a sphere centered at the origin. This is obviously true of any reciprocal-lattice point hkl . The sum total of all reciprocal-lattice points, therefore, comprises a set

of concentric spheres of radii σ_{hkl} centered at an origin which lies on the sphere of reflection. These reciprocal-lattice spheres, therefore, intersect the sphere of reflection in small circles. Since a diffracted beam develops whenever a reciprocal-lattice point intersects the sphere of reflection, the diffracted beams form cones emanating from the center of the sphere of reflection, as illustrated in Fig.2 for one such cone.

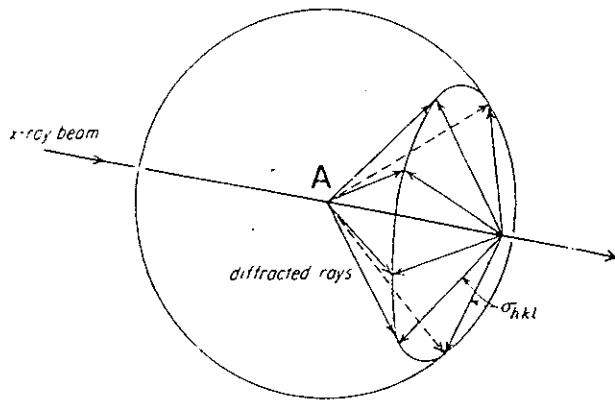


Fig.2.^[1]

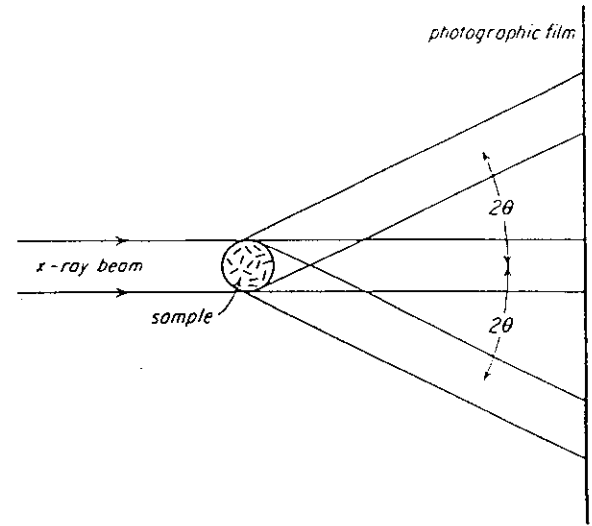


Fig.3.^[1]

The principles involved in the production of a powder diagram can be appreciated by considering the simplified experimental arrangement shown in Fig.3. An X-ray beam is defined by the pinhole system, just described. A photographic film is then placed normal to the x-ray beam. The powder sample is introduced into the path of the x-ray beam. As the beam travels through the powder sample, it meets thousands of powder grains, each a tiny crystal in a different orientation. Among these grains many are so oriented that a particular set of planes (hkl) makes the appropriate glancing angle θ (for the plane) with the x-ray beam. Such grains are in position to reflect x-rays. The reflection occurs in a direction making an angle 2θ with the direct x-ray beam. The locus of directions making an angle 2θ with a given direction is a cone of half opening angle 2θ . For each solution of the Bragg equation

$$\theta = \sin^{-1} \left(\frac{\lambda \cdot n}{2 \cdot d_{hkl}} \right) \quad (1)$$

there exists such a cone.

We remember that in a space lattice each Miller index triplet is represented by a series of parallel equispaced planes containing all the lattice points. In actual crystals these planes are the loci of the atomic or molecular units of the crystal pattern. d_{hkl} , the interplanar spacing, is the perpendicular distance between successive planes of a series.

A simple way to record the diffraction pattern of a polycrystalline material is by placing a film perpendicular to the incident X-ray beam. The diffraction cones will, in this case, give rise to a series of concentric rings each satisfying the Bragg law (Fig 4).

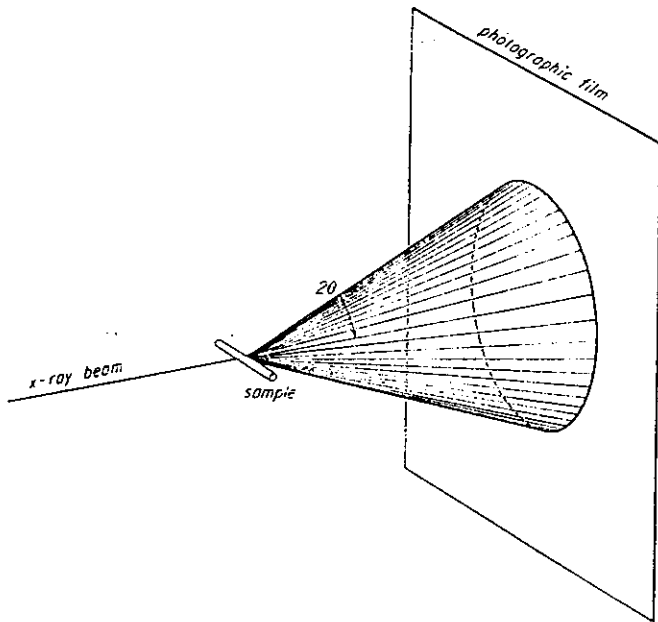


Fig.4.^[1]

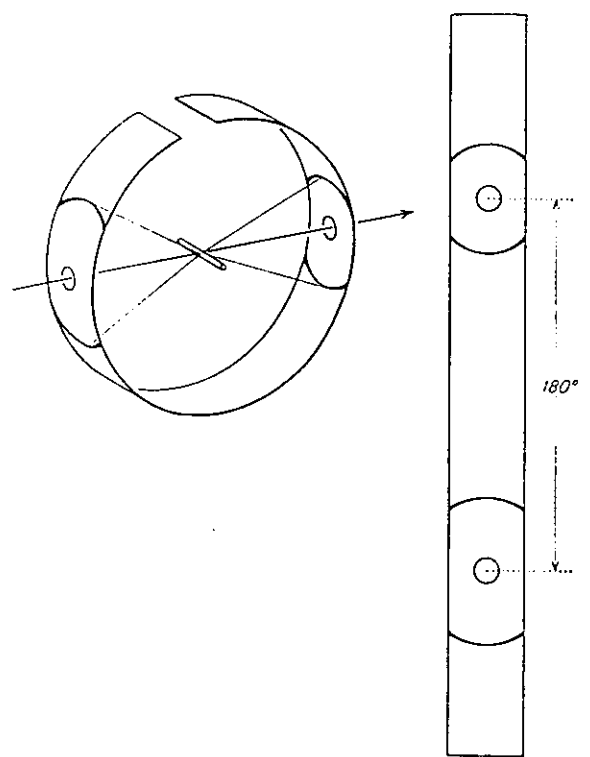


Fig.5.^[1]

Alternatively, a narrow strip of film can be placed on the cylinder centred at the sample. In this case, the cones will generate concentric arcs, which are segments of the rings, on the strip (Fig.5).

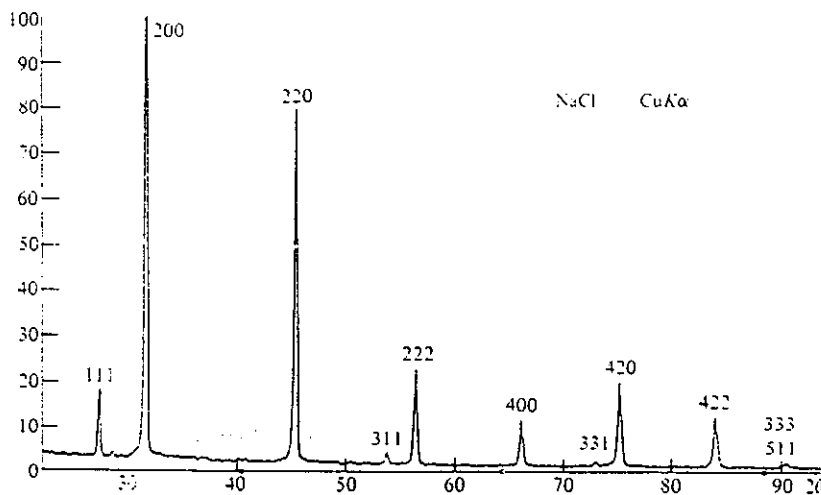


Fig.7^[2]

A final possibility is to reduce the strip to a line, that is simply to record the position and the intensity of the diffracted radiation on any plane that contains the incident X-ray beam. In this last case one only measures, the radius of the cone and the

diffracted intensity at a single

position. If the sample can be considered perfectly isotropic this single measurement is sufficient to completely characterize the diffraction pattern. The parameters reported are 2θ , that is the angle made by any vector with origin in A (see Fig.2) and lying on the diffraction cone surface and the

incident X-ray beam, and the relative intensity of the radiation along any direction on the cone (Fig.7).

Let us consider, now, a diffracting object in which the relative positions of the atoms are fixed. We assume that the object rotates in such a manner that all possible orientations with respect to the incident beam are equally probable. We also assume that this motion is sufficiently rapid so that one observes only the average diffracted intensity. This is equivalent to observing the diffraction by a collection of identical objects with random orientations and positions. We shall call such an object a perfect powder.

The Debye formula for the intensity is

$$I = \sum_m \sum_n f_m f_n \frac{\sin(hr_{mn})}{hr_{mn}} \quad (2)$$

Let us consider an object composed of atoms or of identical group of atoms with structure factor F . We consider first in Eq.(2) the N terms related to a given atom, and we notice that each pair is counted twice, the distance r_{mn} being equal to r_{nm} . We shall call r_z the interatomic distances in the object. There are $[N(N-1)]/2$ of these. According to the Debye formula the interference function is

$$F(h) = \frac{I}{NF^2} = 1 + \frac{2}{N} \sum_z \frac{\sin(hr_z)}{hr_z} \quad (3)$$

The powder diagram depends only on the lengths of all the interatomic vectors, it does not depend on their mutual orientations.

The Debye formula applies, in particular to a crystalline powder of identical particles. Let us consider grains of a simple cubic crystal having the form of cubes measuring $(n-1)a$, a being the lattice parameter of the unit cell. The scattering power is

$$F(h) = 1 + \frac{6n^2(n-1)}{n^3} \frac{\sin(ha)}{ha} + \frac{12n(n-1)^2}{n^3} \frac{\sin(ha\sqrt{2})}{ha\sqrt{2}} \quad (4)$$

This equation gives the intensity of the Debye-Scherrer powder diagram, taking into account the shapes of the lines due to the size of the elementary crystal. It is not obvious from this equation that the intensity is zero everywhere, except in the immediate neighbourhood of the lines corresponding to the Bragg angles. A complex calculation shows, however, that this expression is equivalent to that derived from the classical expression valids for a small crystal having the shape of a parallelepipedon with edges N_1a_1 , N_2a_2 , N_3a_3 parallel to the crystal axes $a_1a_2a_3$:

$$I = I_e F^2 \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{N}_1 \mathbf{a}_1}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1} \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{N}_2 \mathbf{a}_2}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2} \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{N}_3 \mathbf{a}_3}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3} \quad (5)$$

where

$$\left| \frac{\mathbf{s} - \mathbf{s}_0}{\lambda} \right| = \frac{2 \sin \theta}{\lambda}$$

$y = (\sin^2 N x) / \sin^2 x$ is a peak function essentially zero everywhere except in the immediate vicinity of $x = n\pi$ where it rises to high maxima and the peaks are, accordingly, higher and sharper when N increases. Hence the intensity I will be essentially zero unless the three quotients are simultaneously close to their maximum values. For I to be a maximum, we must simultaneously satisfy the three conditions

$$(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1 = h' \pi$$

$$(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2 = k' \pi$$

$$(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3 = l' \pi$$

where h' , k' , l' are three integers. Rearranged and written in the form below, these are called the 3 Laue equations:

$$(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1 = h' \pi$$

$$(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2 = k' \pi$$

$$(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3 = l' \pi$$

(6)

Since a diffracted beam exists only if the 3 Laue equations are simultaneously satisfied, these three equations together must be equivalent to the Bragg law.

In the powder method, a monochromatic beam falls upon a powder sample containing an enormous number of very small crystal having completely random orientations. For any set of planes hkl with spacing d_{hkl} , there will be a few crystals whose planes hkl make the correct angle with the primary beam to allow a Bragg reflection such that the corresponding powder pattern shows a sequence of line profile characteristic of the crystalline system investigated.

Experimentally a diffraction line profile is the result of the convolution of a number of independent contributing shapes, some symmetric and some asymmetric. It can be represented as :

$$h(x) = \int g(x') f(x - x') dx' + \text{background} = g(x) * f(x) + \text{background}$$

where x measures the angular deviation of any point from the theoretical scattering angle $2\theta_0$, x' is the variable of integration in the same x domain, $g(x)$ is the instrumental profile function, $f(x)$ is the intrinsic diffraction profile function, and $h(x)$ is the resulting observed profile function.

Recently powder profile refinement methods devoted

1) to deriving structural parameters such as atomic coordinates in the unit cell, thermal motion etc.

2) to extract physical information such as : phase identification , crystallite size, lattice disorder have been developed. In order to describe the experimental profiles, symmetric analytical profile functions such as: Gaussian, Lorentzian, pseudo-Voigt, Pearson VII etc. have been used

Eq. 5 can be used to show the effect on the diffraction pattern of various crystal imperfections such as small crystallite size, strains, and faulting. Since it is the simplest kind of imperfection we shall deal mostly with the effect of small crystallite size remembering that the diffraction line becomes broader as the crystal size decreases.

The first treatment of particle size broadening was due to Scherrer.

He showed that

$$L = \frac{K\lambda}{B(2\theta) \cdot \cos\theta} \quad (7)$$

wherein θ and λ have their usual meanings, L is the mean dimension of the crystallites composing the powder, $B(2\theta)$ is the full width in radians subtended by the half maximum intensity width of the powder pattern peak, and K a constant approximately equal to unity and related to the crystalline shape.

A more general treatment was proposed by Warren and Averbach (Fourier method) in which some information about strains can be also provided. It can be summarized as follows:

the experimental broadened profile has to be deconvoluted from the instrumental and spectral effects in order to obtain the corrected Fourier transforms $A(L)$ (L is the variable in the direct space). According to Warren and Averbach the coefficients $A(L)$ (or the Fourier transforms) are the products of size coefficients $A_s(L)$ and distortion coefficients $A_d(L)$:

$$A(L) = A_s(L)A_d(L) \quad (8)$$

where $A_s(L)$ is independent of the peak order and $A_d(L)$ is dependent upon the order of the diffraction peak. If at least two orders of reflections of the same plane family are known, by means of the following expression:

$$\ln A(L, 1/d_{hkl}^2) = \ln A_s(L) - 2\pi^2 \langle \epsilon^2(L) \rangle L^2 / d_{hkl}^2 \quad (9)$$

where hkl are the Miller indices, $\langle \epsilon^2(L) \rangle$ is the squared microstrain averaged over all distances L , and d_{hkl} is the interplanar spacing, it is possible to separate the crystalline size contribution from that of lattice distortion.

For very small cluster containing few atoms it is preferable to calculate the pattern from the Debye formula. If we consider a liquid, it has no structure with respect to a fixed origin since the atoms are continually moving about. In an amorphous solid (glasses, glassy metals, resins,

unoriented solid polymers), the atoms have permanent neighbours but there is no repeating structure, only local configurations. Although there is no sharp dividing line between crystalline and so called amorphous materials, for clarity in this discussion we somewhat arbitrarily designate as *crystalline* those materials characterized by three-dimensional periodicity over appreciable distances, say, of the order of six or more unit translations. Conversely, materials possessing only one or two-dimensional, or lesser, degrees of order are referred to as *amorphous*.

Fig. 8 is a two dimensional illustration of the difference between the arrangement of atoms in a hypothetical crystal A and glass B of the same chemical composition, A_2O_3 .

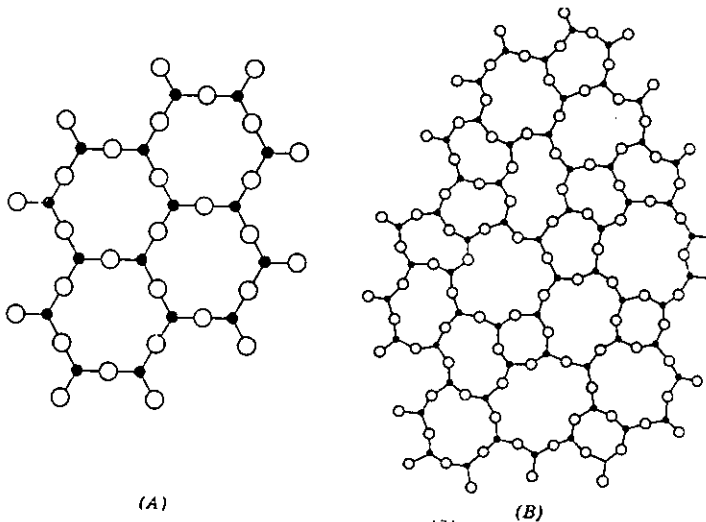


Fig. 8.^[3]

However, atoms have well-defined sizes and closest distances of approach, and hence both liquids and amorphous solids have definite structures relative to an origin at the center of an average atom. This type of structure is expressed by a Radial Distribution Function (RDF) $4\pi r^2 \rho(r)$ such that $4\pi r^2 \rho(r) dr$ is the average number of atom centers between distances r and $r+dr$ from the center of an average atom.

Eq. (2) makes it possible to establish the correct atomic configuration by inverting the experimental intensity function by means of the Fourier integral theorem as first suggested by Zernike and Prins, and so to obtain the RDF of the specimen.

The application of the Fourier integral theorem is perfectly straightforward in the case of a substance consisting of only one kind of atom. Then Eq.(2) becomes

$$I = Nf^2 \sum_m \frac{\sin(hr_{mn})}{hr_{mn}} \quad (10)$$

if it is assumed that the environment of one atom is the same as that of any other atom.

Since in performing the summation of eq.(10) each atom in turn becomes the reference atom, there are N terms due to the interaction of each atom with itself. The value of each of these terms is unity, since in the limit as $r_{mn} \rightarrow 0$, $(\sin hr_{mn})/hr_{mn} \rightarrow 1$. So eq.(10) may be written

$$I = Nf^2 \left(1 + \sum_m \frac{\sin(hr_{mn})}{hr_{mn}} \right) \quad (11)$$

if it be understood that the summation excludes the origin atom. The distribution of atoms about any reference atom may now be regarded as a continuous function and the summation replaced by a integral

$$I = Nf^2 \left[1 + \int_0^{\infty} 4\pi r^2 \rho(r) \frac{\sin(hr)}{hr} dr \right] \quad (12)$$

Here $\rho(r)$ is the number of atoms per unit volume at a distance r from the reference atom, and $4\pi r^2 \rho(r) dr$, as reported above, is the number of atoms contained in a spherical shell of radius r and thickness dr . Letting ρ_0 be the average density of atoms in the sample, eq (12) may be rewritten as

$$I = Nf^2 \left\{ 1 + \int_0^{\infty} 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin(hr)}{hr} dr + \int_0^{\infty} 4\pi r^2 \rho_0 \frac{\sin(hr)}{hr} dr \right\} \quad (13)$$

The integral of the last term of eq.(13) represents the scattering by a hypothetical object of the same form as the specimen but of rigorously uniform electron density. This is the central scattering, which occurs at such small angles as to be unresolvable from the direct beam. Hence, if attention is limited to experimentally observable intensities, $i(h)$, eq.(13) can be simplified to the form

$$\frac{I}{Nf^2} - 1 = \int_0^{\infty} 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin(hr)}{hr} dr$$

By means of the Fourier integral theorem, this expression can be transformed to

$$r[\rho(r) - \rho_0] = \frac{1}{2\pi^2} \int_0^{\infty} hi(h) \sin(hr) dh$$

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\infty} hi(h) \sin(hr) dh$$

where

$$i(h) = \frac{I}{Nf^2} - 1$$

The case of the presence of more than one kind of atom will be treated in section II.

References

*This lecture is based on the following books:

- 1) L.V.Azaroff and M.J.Buerger, The powder method (1958). McGraw-Hill, New York.
- 2) B.E.Warren, X-Ray Diffraction (1969). Addison-Wesley, Reading.
- 3) H.P.Klug and L.E.Alexander, X-ray diffraction procedures (1974). Wiley, New York.
- 4) A.Guinier, X-ray Diffraction (1963). Freeman, San Francisco.
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POWDER DIFFRACTION II

In these last years, dedicated powder diffractometers are in operation at many synchrotron sources. In contrast to conventional radiation source, the main properties of synchrotron radiation are

- 1) the extremely good instrumental resolution over extended angular ranges (for example, full widths at half maximum of $<0.01^\circ$ out to a d-spacing of 1\AA at a wavelength of 0.7\AA),
- 2) excellent peak-to-background discrimination,
- 3) peak shapes which are very well described by the commonly-used pseudo-Voigt function (including a simple and reliable asymmetry correction for axial divergence at lower angles),
- 4) high brightness (large amount of flux in a well collimated beam)
- 5) an intense continuous wavelength distribution spectrum, from which monochromatized X-radiation can be selected and the consequent possibility of using anomalous scattering as a general probe of cation distribution for elements with $Z > 35$.

As an example Fig.1 shows the variation in instrument-only contributions to the peak full-width-at half-maximum (FWHM) as a function of diffraction angle for a number of modern neutron and X-ray diffractometers.

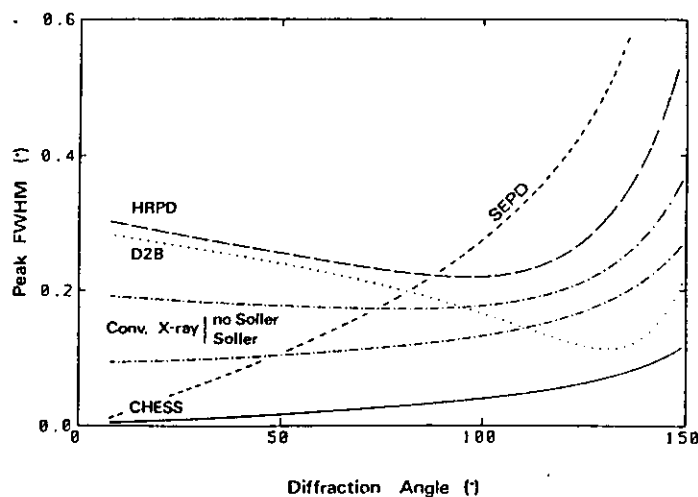


Fig.1 Variation in the instrumental-only peak FWHM as a function of diffraction angle (2θ) for several neutron and X-ray diffractometers. The curves represent the following instruments: long --- HRPD(CW neutron) at Lucas Heights; --- D2B(CW neutron) at the ILL; short --- SEPD(TOF neutron) at the ANL; --- conventional (X-ray) Bragg-Brentano with (lower) and without (upper) diffracted-beam Soller slits; — synchrotron (X-ray) Bragg-Brentano at CHES.^[1]

In this part, some of the most important aspects will be treated in relation to their applications in Material Science. In particular, beside some general considerations on the application of the broadening analysis and kinetics of crystallization, the Rietveld method, thin films analysis, anomalous scattering and their relative applications will be briefly reported.

RIETVELD METHOD^[1]

In the mid-sixties, it became apparent to various diffractionists that much more information could be obtained from a powder pattern if the full power of computers could be applied to full-pattern analysis. The recognized point was that in a step-scanned pattern, for example, there was some information attached to each intensity at each step in the pattern, even if it were the negative information that there was no Bragg-reflection intensity there or the partial and the scrambled information that the intensity at a step was the sum of contributions from the details of several Bragg reflections. It was Rietveld who first worked out computer-based analytical procedures to make use of the full information content of the powder pattern.

In the Rietveld method the least-squares refinements are carried out until the best fit is obtained between the entire observed powder diffraction pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models for the crystal structure(s), diffraction optics effects, instrumental factors, and other specimen characteristics (e.g. lattice parameters) as may be desired and can be modelled.

A powder diffraction pattern of a crystalline material may be thought of as a collection of individual reflection profiles, each of which has a peak height, a peak position, a breadth, tails which decay gradually with distance from the peak position, and an integrated area which is proportional to the Bragg intensity, I_K , where K stands for the Miller indices, h, k, l . I_K is proportional to the square of the absolute value of the structure factor, F_K^2 . In all powder diffraction patterns but those so simple that the Rietveld method is not needed in the first place, these profiles are not all resolved but partially overlap one another to a substantial degree.

If y_i is the numerical intensity value recorded at each of equal increments (steps), i , in the pattern the quantity minimized in the least-squares refinement is the residual, S_y :

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$

where

$w_i = 1/y_i$; y_i = observed intensity at the i th step; y_{ci} = calculated intensity at the i th step, and the sum is overall data points.

It is a crucial feature of the Rietveld method that no effort is made in advance to allocate observed intensity to particular Bragg reflections nor to resolve overlapped reflections. Consequently, a reasonably good starting model is needed. The method is a structure refinement method.

Typically, many Bragg reflections contribute to the intensity, y_i , observed at any arbitrary chosen point, i , in the pattern. The calculated intensities y_{ci} are determined from the $|F_k|^2$ values calculated from the structural model by summing of the calculated contributions from neighbouring (i.e. within a specified range) Bragg reflections plus the background:

$$y_{ci} = s \sum_K L_K |F_k|^2 \phi(2\theta_i - 2\theta_k) P_K A + y_{bi}$$

where

s is the scale factor,

K represents the Miller indices, hkl , for a Bragg reflections,

L_K contains the Lorentz, polarization, and multiplicity factors,

ϕ is the reflection profile function,

P_K is the preferred orientation function,

A is the absorption factor,

F_K is the structure factor for the K th Bragg reflection, and

y_{bi} is the background intensity at the i th step.

The usual refinable parameters are listed as follow:

For each phase present

x_i y_i z_i B_i N_i (x_i , y_i and z_i are position coordinates, B_i is an isotropic thermal parameter, and N_i is the site-occupancy multiplier, all for the i th atom in the unit cell)

Scale factor (note quantitative phase analysis possibility)

Specimen-profile breadth parameters

Lattice parameters

Overall temperature factor (thermal parameter)

Individual isotropic or anisotropic thermal parameters

Preferred orientation

Crystalline size and microstrain (through profile parameters)

Global

2 θ -Zero

Instrumental profile

Profile asymmetry

Background

Wavelength

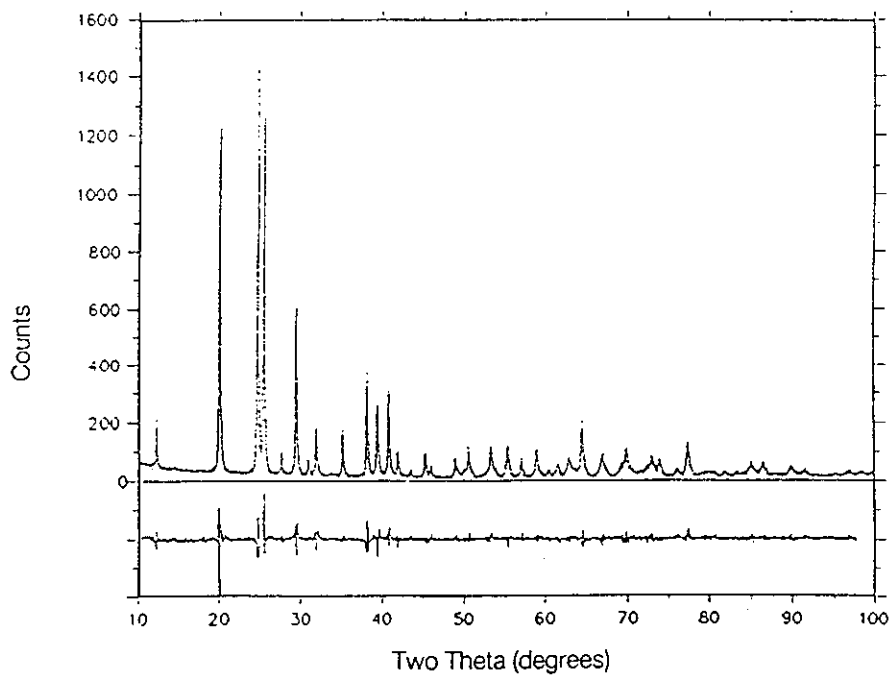
Specimen displacement

Specimen transparency

Absorption.

As an example, in Fig.2 the final fitted profile of Lithium Disilicate, using Pearson VII functions, is reported

Fig.2.^[2]



In the presence of multiple phases, Rietveld analysis can provide very accurate estimates of the relative and/or absolute abundances of the component phases according to:

$$W_p = \frac{S_p(ZMV)}{\sum_{i=1}^n S_i(ZMV)}$$

where W is the relative weight fraction of phase p in a mixture of n phases, and S , Z , M and V are, respectively, the Rietveld scale factor, the number of formula units per unit cell, the mass of the formula unit (in atomic mass units) and the unit cell volume (in \AA^3).

THIN FILM^[3-4]

X-ray diffraction methods are widely used for the characterization of thin films. The increasing use of thin films with special tailored properties, for example for electronic devices, has stimulated the need for improved characterization methods. The properties are determined by the thin-film material and its crystal structure. The microstructure is critically dependent on the various parameters used in the deposition of the film, and their effect on the required properties can be followed by x-ray diffraction. It is well known that thin films are usually not uniform, and indeed it may be desirable to purposely vary the microstructure as a function of the thickness to obtain the desired properties. Methods that obtain diffraction patterns from different film depths are now essential for complete structural characterization. The high intensity of a Synchrotron radiation is an important factor in measuring the weak scattering from thin films.

REFLECTION GEOMETRY

In the microstructural analyses of thin films, special experimental techniques have to be employed to obtain diffraction patterns with sufficient statistical accuracy in a reasonable counting time. Since films and coatings are normally supported by a relatively thick substrate, one is forced to use the reflection geometry, shown in Fig.3

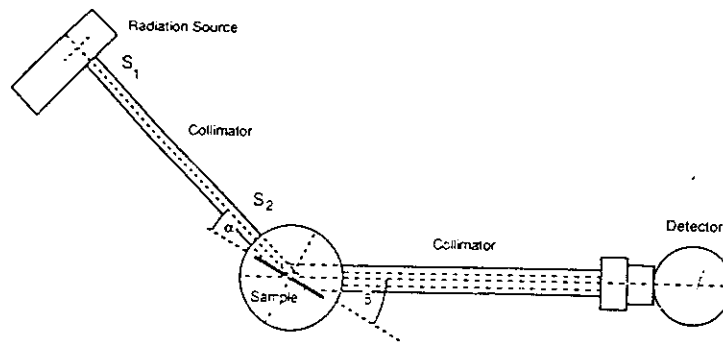


Fig.3 Reflection geometry with parallel X-ray beam, defined by the incident beam slits S_1 and S_2 . In the fixed incidence: 2θ scanning, the sample surface makes a fixed angle α with the direction of the incident beam. The detector sees the same sample area at any angle of reflection β . The scattering angle is defined as $2\theta = \alpha + \beta$. In $\theta:2\theta$ scanning, the angle of incidence $\alpha = \beta$ and the sample surface continuously bisects the angle 2θ , so that $\beta = \theta$.^[3]

In any case, the conventional x-ray methods, when used for thin films, the x-ray beam usually penetrates the entire film making it impossible to follow structural variations as a function of film depth.

The depth of x-ray penetration into the film depends on the angle of incidence α . When the incident angle becomes $<$ than a certain angle α_c , specific of the material, the depth is very small (usually about 50-100Å) The critical angle α_c for the total reflection is given by

$$\alpha_c = (2\delta)^{1/2} = 1.6 \times 10^{-3} \rho \lambda$$

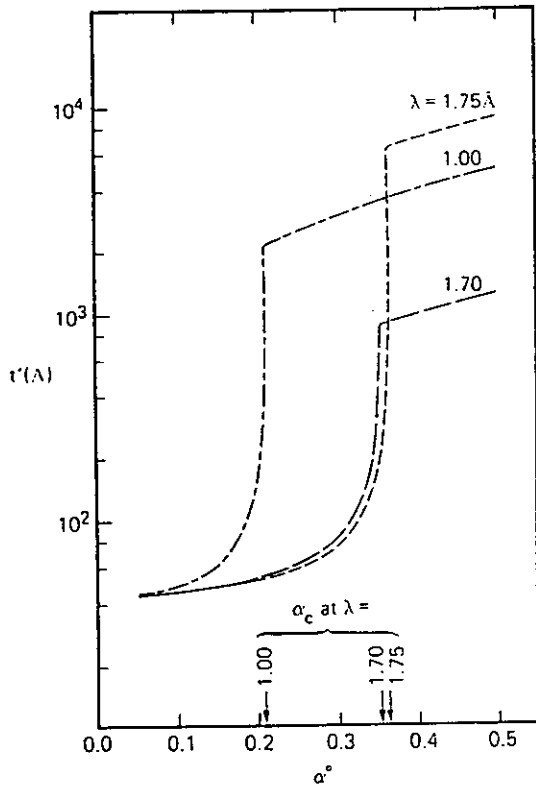


Fig.4.^[4]

where α_c is in radians, ρ is the density in gcc^{-1} and λ is the wavelength in Å . This ignores anomalous dispersion, which has a significant effect even on the long wavelength side of the absorption edge. For $\alpha < \alpha_c$ the penetration depth t' is determined by the total external reflection process and is given by

$$t' = \lambda / [2\pi(\alpha_c^2 - \alpha^2)^{1/2}] \quad (1)$$

The thinnest layer that can be sampled is determined by the density of the film.

For $\alpha > \alpha_c$ the penetration depth is dependent on the linear absorption coefficient μ_l :

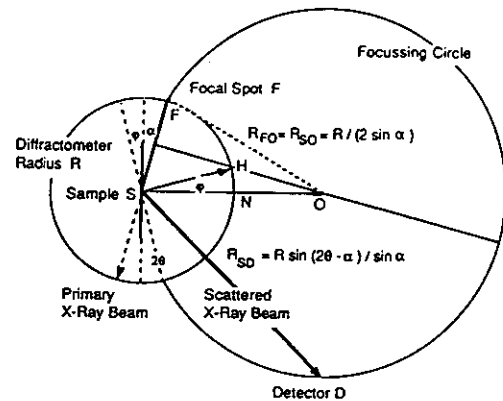
$$t' = 2\alpha / \mu_l \quad (2)$$

Fig.4 shows the penetration depth in the iron oxide film as a function of α and λ as calculated by eqs.(1) and (2).

Seemann-Bohlin Geometry

For many years, researchers have employed the Seemann-Bohlin geometry (see Fig.5) for the measurements of the powder patterns of thin films.

Fig.5 Focussing Seeman-Bohlin diffractometer. The sample S remains fixed at constant angle of incidence α , while the detector slit moves along SD by the amount $R_{SD} = R \sin(2\theta - \alpha) / \sin \alpha$ to remain on the focussing circle of radius $R_{FO} = R_{SO} = R / (2 \sin \alpha)$, where R is the radius of the diffractometer.^[3]

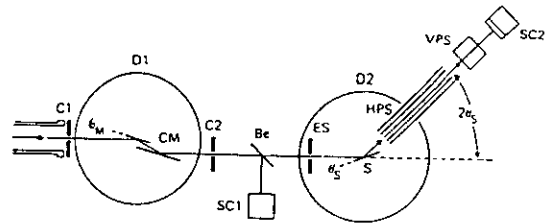


In the Seeman-Bohlin focusing geometry, the specimen is set at a fixed small angle (about 5° minimum) and the detector is moved around the focussing circle by a special linkage. However mechanical restriction prevents using smaller angle required for grazing incidence and any departure from the strict focusing requirements causes large geometrical aberration in the pattern.

Parallel Beam reflection geometry

Because of the limitations of the Seeman Bohlin geometry, it might be advantageous to adopt the parallel beam geometry with a fixed angle of incidence α (in Fig.6 θ_s) as shown in Fig.6.

Fig.6 Parallel beam X-ray optics used in $\theta:2\theta$ and grazing incidence: 2θ scanning.^[4]



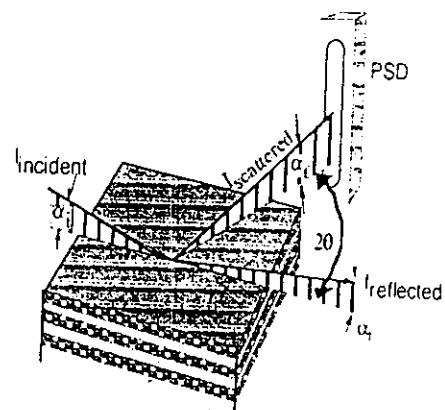
Since the specimen has a finite dimension, say 30 mm in width, one must limit the width of the primary beam to 1 mm in order to reach a low incidence angle $\alpha = 2^\circ$. In this case, the detector is always looking at the entire irradiated area, and one must install a set of Soller slits whose blades are placed perpendicular to the diffraction plane so that the diffraction angle is well defined.

Grazing Incidence Scattering

As shown above, if one wishes to employ the effect of total reflection of the incident beam for the analysis of angstrom thick layers, one must reduce the angle of incidence α to a value less than the critical angle α_c which is only a fraction of one degree. Thus, the method of grazing incidence scattering (or diffraction) requires a very narrow x-ray beam because of the finite sample size and a strong primary beam, available with synchrotron sources. In this technique, one can scan the diffracted beam in the same way as presented in Fig.3, with the diffraction plane, containing the incident and diffracted beams, perpendicular to the specimen surface (method 1), i.e., using the parallel beam geometry.

One can also scan the diffracted beam almost parallel to the specimen surface as shown in Fig.7, i.e., the incident beam I_{incident} strikes the specimen at an angle $\alpha_i < \alpha_c$, and the diffracted beam is detected at a second grazing angle α_f . The diffraction angle 2θ is defined as the angle between the projections of α_i and α_f onto the specimen surface (method 2).

Fig.7 Schematic diagram showing grazing incidence scattering X-ray diffraction.



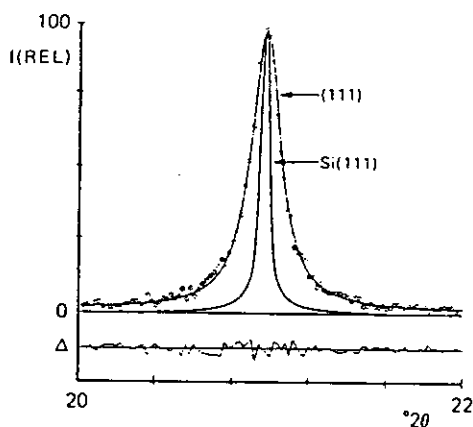


FIG.8.^[4]

As an example in Fig.8 are reported the grazing incidence diffraction profiles, $\alpha=0.25^\circ$, $\lambda=1.75\text{\AA}$, of unbroadened Si(111) powder and broadened 6.5h annealed iron oxide film (111): peak intensities normalized. Outer profile fitted with symmetrical Lorentz function.

ANOMALOUS X-RAY SCATTERING^[5-6]

Even if the usefulness of the anomalous X-ray scattering has also been confirmed in structural investigation of polycrystalline samples (some examples will be reported during the lecture), we focalize our attention in *Amorphous Materials* (in which the atomic arrangement is not spatially periodic) containing more than two kinds of atoms in order to evaluate the partial radial distribution function

The diffraction pattern from an amorphous sample (i.e. a glass) exhibits broad features, indicating the lack of translational symmetry in its structure. The quantity obtained from a conventional scattering experiment is the radial distribution function (RDF), which is a description of the average environment of an atom, for example, in a glass. The RDF is defined as $4\pi r^2\rho(r)$, where $\rho(r)$ is the radial density function and r is the radius; $\rho(r)$ is the average number density of atoms at a distance r from an average atom at the origin. The RDF, therefore, is the number of atoms in a shell of unit thickness at a distance r . The number of neighbours coordinating a central atom is obtained by integrating a peak in the RDF, and the average distance of these neighbours is obtained from the peak position.

Even in one-component system, the interpretation of the RDF is difficult because the local structure is spherically averaged. In a multicomponent system, the problem is even more complex because the average environment portrayed by the RDF might bear little resemblance to the actual environment of any given component.

Anomalous scattering experiments permit species-specific distribution functions to be obtained, which give a more direct view of the amorphous structure (such structural information is very similar to the results by EXAFS measurements).

When the X-ray energy is close to an absorption edge of an atom, the X-ray scattering factor changes significantly through the anomalous scattering factors (ASF's) f' and f'' . For example, the

scattering factor of Se is reduced from its maximum value by approximately 10 electrons at the K absorption edge energy. Therefore, Se (atomic number $Z=34$) scatters more like Cr ($Z=24$). Suppose scattering patterns are obtained from an Ag-Ge-Se glass at two X-ray energies close to the Se K absorption edge. The scattering behaviour of Se is different at each energy, but the behaviour of Ge and Ag is the same. The difference between the two patterns can be related to the distance correlations involving Se atoms.

The result of this type of experiment is the *difference distribution function* (DDF) around Se. The DDF is $4\pi r^2 \rho_{Se}(r)$, where $\rho_{Se}(r)$ is the density of atoms at a distance r from a central Se atom.

The idea of obtaining structural information from the derivative of the scattered X-ray intensity with respect to energy was first proposed by Shevchik^[7-8]. However, the *differential anomalous scattering* (DAS) technique outlined above was first developed and applied experimentally to amorphous GeSe and glassy GeSe₂ by Fuoss^[9-10].

Because the X-ray energy must be near an absorption edge, the DAS technique cannot be applied to atoms whose atomic numbers are less than 24 (Cr). As the edge energy decreases, the region of reciprocal space that is accessible to measurement becomes smaller, with the effect that the resolution of the DDF in real space is degraded.

The potential of anomalous scattering experiments is not limited to obtaining DDF's. It is possible to obtain the partial distribution function (PDF), in which the intensities of both the central atom and its neighbors are known. The $\alpha\beta$ PDF describes the distribution of β atoms around a central α atom; it is equal to $4\pi r^2 \rho_{\alpha\beta}(r)$, where $\rho_{\alpha\beta}(r)$ is the number density of β atoms at a distance r from an α atom at the origin. The total number α - β distances in the structure is constant, leading to the condition

$$X_{\alpha}\rho_{\alpha\beta}(r)=X_{\beta}\rho_{\beta\alpha}(r)$$

where X is the mole fraction. The RDF and the DDF's are related to the PDF's by

$$RDF = \sum_{\alpha=1}^M X_{\alpha} DDF_{\alpha} = \sum_{\alpha=1}^M X_{\alpha} \sum_{\beta=1}^M PDF_{\alpha\beta}$$

Keating demonstrated how $M(M+1)/2$ independent scattering experiments can be used to determine the same number of independent PDF's. In each experiment, the scattering factors of one or more of the components must be altered in independent way. The energy dependence of the anomalous scattering factors provides one means to accomplish this. If we consider a three components glass, six scattering patterns must be collected, two in the vicinity of the K absorption edge of each component.

The PDF's are difficult to obtain because the independence that can be achieved by varying the anomalous scattering factors is limited. In practice, the results are very sensitive to experimental error.

Anomalous scattering factors

The X-ray scattering factor of an atom is the amplitude and phase of the wave scattered coherently from the atom relative to the amplitude and phase of the wave scattered by an isolated, or free, electron. In general, the atomic scattering factor f is complex and is written as

$$f = f_0(h) + f'(h,E) + if''(h,E)$$

which explicitly states the dependences on E , the X-ray energy, and h , the magnitude of the scattering vector:

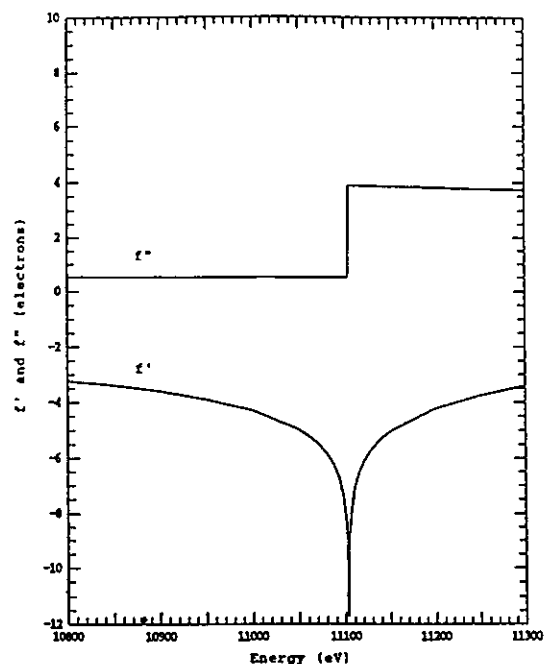
$$h = \frac{4\pi\sin\theta}{\lambda}$$

where 2θ is the scattering angle, and λ is the X-ray wavelength. The quantity f_0 is the scattering factor when the X-ray energy is much greater than the largest ionization energy for the atom. At such energy, all electrons in the atom scatter as if they were free. If the X-ray energy is comparable to or less than the ionization energies of some of the electrons, the ASF's f' and f'' are nonzero. The ASF's correct the amplitude and phase of f_0 for the fact that these electrons do not scatter as free electrons.

Values for f_0 have been calculated from theory for isolated atoms and ions.

The anomalous scattering factors can be calculated theoretically or determined experimentally. The ASF's determined theoretically (see Fig. 9) are quite accurate when the X-ray

Fig.9 Cromer and Liberman calculation of the ASF's for Ge near the Ge L Absorption Edge (11103 eV).^[5]



energy is not close to an absorption edge. However, in the immediate vicinity of the edge, solid state effects cause significant deviations from the isolated atom results. The ASF's used in DAS experiments, therefore, should be measured experimentally.

The method commonly employed for DAS experiments is to use the optical theorem to calculate f'' from a measurement of the absorption cross section as a function of energy; f' is calculated from f'' via the Kramers-Kronig relation.

The optical theorem can be derived by relating the composite effect of the scattering by individual atoms in a substance to the complex index of refraction characterizing the material as a whole. The imaginary part of the index of refraction corresponds to the absorption of a wave as it travels in the material and can be expressed in terms of the total absorption cross section σ . The optical theorem relates f'' to σ :

$$f''(\omega) = \frac{mc\omega\sigma(\omega)}{4\pi e^2}$$

where f'' is in electrons, σ has units cm^2/atom , m and e are the mass and charge of an electron, ω the X-ray angular frequency, and c the speed of light; all units are cgs.

The Kramers-Kronig relation is

$$f'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' f''(\omega')}{\omega_0^2 - \omega'^2} d\omega'$$

in which the integral is understood to be the Cauchy principal value.

RDF Analysis

Under the assumptions of the kinematic theory of X-ray diffraction, the coherently scattered intensity in electron units (eu) from a collection of atoms is

$$I_{\text{eu}}(\mathbf{h}) = \sum_i \sum_j f_i^* f_j \exp(i\mathbf{h} \cdot \mathbf{r}_{ij}) \quad (3)$$

where the summations over i and j are for all atoms in the sample, \mathbf{h} is the scattering vector, \mathbf{r}_{ij} the vector from atom i to atom j , and the asterisk denotes the complex conjugate. The scattering is uniform with respect to sample orientation. Therefore, after taking the spherical average of the experimental term, separating the independent scattering ($i=j$) terms, and grouping the distances between two specific types of atoms together, the equation can be rewritten as

$$I_{\text{eu}}(\mathbf{h}) = \sum_{\alpha=1}^M N_\alpha |f_\alpha|^2 + \sum_{\alpha=1}^M \sum_{\beta=1}^M f_\alpha^* f_\beta \sum_i \sum_j \frac{\sin(\mathbf{h} \cdot \mathbf{r}_{ij})}{\mathbf{h} \cdot \mathbf{r}_{ij}} \quad (4)$$

in which α and β refer to kinds of atoms in an M component system, i and j are now summations over the α and β types respectively, and N_α is the number of α atoms.

Next, the continuous partial density function $\rho_{\alpha\beta}(r)$ is defined in terms of the discrete interatomic distances present in the structure:

$$4\pi r^2 \rho_{\alpha\beta}(r) dr = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \delta(r - r_{ij}) \quad (5)$$

Here, δ is the delta function. At large radii $\rho_{\alpha\beta}(r)$ approaches the average density of b atoms $\rho_{\beta 0}$. Equation (5) is introduced into eq.(4) as the average density $\rho_{\beta 0}$ and the deviation from that density $\rho_{\alpha\beta}(r) - \rho_{\beta 0}$. Warren showed that the contribution from the average density is only significant at small scattering angles, where the intensity is not experimentally measured. The result, neglecting the small angle scattering term, is

$$I_{eu}(h) = \sum_{\alpha=1}^M N_\alpha |f_\alpha|^2 + \sum_{\alpha=1}^M \sum_{\beta=1}^M N_\alpha f_\alpha^* f_\beta \int_0^\infty 4\pi r^2 (\rho_{\alpha\beta}(r) - \rho_{\beta 0}) \frac{\sin(hr)}{hr} dr \quad (6)$$

Defining the partial structure factor as

$$S_{\alpha\beta}(h) = \frac{1}{h} \int_0^\infty 4\pi r (\rho_{\alpha\beta}(r) - \rho_{\beta 0}) \sin(hr) dr \quad (7)$$

and utilizing $N_\alpha \rho_{\alpha\beta} = N_\beta \rho_{\beta\alpha}$ to group dependent density functions together, Eq (6), on a per-atom basis now, becomes

$$I_{eu}(h) - \langle f^2 \rangle = \sum_{\alpha=1}^M \sum_{\beta=\alpha}^M X_\alpha T_{\alpha\beta} \operatorname{Re}[f_\alpha^* f_\beta] S_{\alpha\beta}(h) \quad (8)$$

where the brackets $\langle \rangle$ denote the molar average, X is the molar fraction and $T_{\alpha\beta}$ equals 2 when $\alpha \neq \beta$ and 1 otherwise.

This is the basic equation for amorphous scattering. It breaks the observed scattering pattern into the coherent independent scattering from individual atoms and the structure-dependent scattering due to distance correlations between atoms. The latter is expressed as the weighted sum of $M(M+1)/2$ independent partial structure factors.

The present development has assumed that I_{eu} is the intensity of the coherent scattering. Experimentally, I_{eu} could contain Compton scattering as well. In that case, the Compton scattering must be subtracted from I_{eu} .

If only one scattering pattern is available, no basis exists for distinguishing the separate contributions of the partial structure factors to the total pattern. Let us treat the pattern as if it originated from a structure consisting of identical "average" atoms. The scattering factor of these fictitious atoms will be taken as $\langle f \rangle$. By analogy with eq. (8), we write

$$I_{eu}(q) - \langle f^2 \rangle = \langle f \rangle^2 S(h) \quad (9)$$

where, with reference to eq.(7), the total structure factor S is related to the real space structure by

$$S(h) = \frac{1}{h} \int_0^{\infty} 4\pi r (\rho(r) - \rho_0) \sin(hr) dr \quad (10)$$

In effect, eqs. (9) and (10) define $S(h)$ and $\rho(r)$. From eq. (10), it is apparent that the two functions are related by a Fourier sine transform. After obtaining $S(h)$, from experimental data using eq.(9), the reduced RDF, $G(r)$, is calculated as

$$G(r) = 4\pi r (\rho(r) - \rho_0) = \frac{2}{\pi} \int_0^{\infty} h S(h) \sin(hr) dh \quad (11)$$

From $G(r)$, the radial density function $\rho(r)$ and the RDF $4\pi r^2 \rho(r)$ can be obtained.

The reduced RDF of a multicomponent system describes the structure in terms of fictitious atoms, which are defined by the average atomic scattering factor. The relationship of $G(r)$ to the $\rho_{\alpha\beta}(r)$'s, which describe the correlations of the actual atoms in the structure, becomes clear by equating eq.(7) to eq.(8) and Fourier transforming. The results is

$$G(r) \approx \sum_{\alpha=1}^M \sum_{\beta=\alpha}^M X_{\alpha} T_{\alpha\beta} \frac{Z_{\text{eff},\alpha} - Z_{\text{eff},\beta}}{\langle Z_{\text{eff}} \rangle^2} G_{\alpha\beta}(r) \quad (12)$$

in which $Z_{\text{eff}} = Z + f$, Z being the atomic number. The reduced PDF is defined as

$$G_{\alpha\beta}(r) = 4\pi r (\rho_{\alpha\beta}(r) - \rho_{\beta 0}) = \frac{2}{\pi} \int_0^{\infty} h S_{\alpha\beta}(h) \sin(hr) dh \quad (13)$$

According to eq.(12), $G(r)$ contains contributions from each $G_{\alpha\beta}(r)$, weighted according to the composition and the scattering ability of the atoms involved.

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